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(54) **Light diffuser composition.**

- (57) A light diffuser composition contains
- a) from 0.1 to 30 weight parts of inorganic particles having an average particle diameter of from 0.1 to 1 micrometer and a refractive index of from 1.9 to 3.2 and
 - b) from 1 to 150 weight parts of polymeric particles having a core/shell morphology with a core of a rubbery vinyl polymer and one or more shells, which particles contain at least 15% of a polymerized alkyl acrylate or alkyl methacrylate, based on the total weight of the particles.
- The light diffuser composition is useful for preparing a polymer composition which contains a thermoplastic polymer and
- a) from 0.001 to 0.3% of the inorganic particles a) and
 - b) from 0.01 to 1.5% of the polymeric particles b).
- Molded articles can be produced from the polymer composition which are particularly useful in lighting applications.

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The present invention relates to a light diffuser composition and its use for imparting light diffusing properties to a thermoplastic polymer. The present invention further relates to a polymer composition containing the novel light diffuser composition and to a compounded composition or molded article produced therefrom.

It is well known to incorporate light diffusers into thermoplastic, transparent polymers. The light diffusers are generally white. When light diffusers are incorporated into a thermoplastic polymer, the polymer composition and articles produced therefrom have light diffusing properties. Usually the resulting colors of these composites are called opalescent colors. They are semi-transparent or translucent to visible light, that is, they scatter transmitted light so that the light source is not visible. Light diffusing polymer compositions may be formed into sheets or films of various thicknesses, or into more complex shapes, such as lamp covers like globes etc.

Light diffusing polymer compositions are widely used by the lighting industry for producing luminaires, like fixed luminaires, road and street lighting, emergency lighting, etc. Accordingly, one important property of light diffusing polymer compositions and articles produced therefrom is a high resistance to thermal aging, particularly a high color stability when exposed to elevated temperatures over an extended time period.

It is known to incorporate certain inorganic additives into polymer compositions in order to impart to the compositions light-diffusing properties.

British patent specification 1,595,426 disclose plastics containing a translucent organic polymer and a white pigment which appear white in reflected and transmitted light. The refractive index n_o of the polymer is in the range of from 1.4 to 1.65 and the refractive index n of the pigment is in the range of from 1.7 to 2.9. Exemplary of white pigments are for example titanium phosphate, lead hydrogen phosphate, zinc oxide, zinc sulfide, magnesium titanate, calcium titanate, titanium dioxide, etc.

German patent 22 51 708 teaches it to be known that white pigments, such as titanium dioxide, zinc sulfide or zinc oxide provide articles produced from organic polymers with an milky white color. The German patent teaches that such pigmented articles have such a low light transmittance that they are not useful as lamp covers. If only a small amount of such pigments is used, they do not scatter the light. German patent 2 251 708 teaches that barium sulfate which has isometrical particles of an average size of 2 to 12 micrometer, preferably of 4 to 9 micrometer, imparts good light-diffusing properties to thermoplastic polymer compositions. Unfortunately, the incorporation of inorganic additives of such a large particle size into thermoplastic polymer compositions has the effect that molded articles produced from such compositions have an uneven surface. Pits and holes can be observed in the surface of the molded articles which are caused by the large particle size of barium sulfate. Furthermore, it is difficult to disperse these inorganic additives evenly in the thermoplastic polymer.

German Offenlegungsschrift DE-A-2,019,325 discloses that the addition of pigments, for example inorganic oxides, such as titanium dioxide, sulfides, such as zinc sulfide, or salts, such as barium sulfate, cause a certain degradation of polycarbonate in the presence of humidity. German Offenlegungsschrift DE-A-2,019,325 suggests stabilization of pigmented polycarbonates by incorporating epoxy groups containing vinyl copolymers into the polycarbonates. A preferred vinyl copolymer is a copolymer of glycidyl methacrylate, methyl methacrylate and styrene. Alternatively, German Offenlegungsschrift DE-A-2,105,487 suggests stabilization of pigmented polycarbonates by incorporating vinyl polymers free of epoxy groups into the polycarbonates. Preferred vinyl polymers are homo- or copolymers of acrylonitrile or methacrylonitrile, derivatives of acrylic or methacrylic acid, such as the methyl, ethyl or butyl esters of acrylic acid, or polymers of alkenyl aromatic compounds, such as styrene or alpha-methyl styrene. The stabilized pigmented polycarbonates disclosed in DE-A-2,019,325 and DE-A-2,105,487 contain from 0.5 to 1.5% of the pigment, such as titanium dioxide, by the weight of the polycarbonate and 5-100%, preferably 10-30%, of the stabilizing vinyl polymer, by the weight of the pigment content. Unfortunately, the use of titanium dioxide at such high levels may promote polymer degradation.

Unfortunately, various common inorganic light diffusers are known to be sensitive to heat and oxygen (for example barium sulfate) or to UV light. Therefore, various light-diffusing polymer particles have been suggested to impart light-scattering properties to polycarbonates or other thermoplastic polymers.

From CA Selects: Plastics Manufacture & Processing, Issue 23, 1992, page 16, Abstract 117:193113e, abstracting JP 04,161,448, light-diffusing polycarbonate compositions are known which comprise 90-99.95% of aromatic polycarbonates and 0.1-10% of spherical particles with an average diameter of 5 to 100 micrometers consisting of powdered titanium dioxide coated with cross-linked cyclohexylmaleimide-styrene copolymers I) containing 10-90% cyclohexylmaleimide. A blend of a 99.9% of lupilon S 3000 (trademark) and 0.1% Techpolymer MR 636 (powdered titanium dioxide coated with copolymer I) is injection-molded at 280°C to give a specimen with light transmission of 70% and diffused light transmission of 40%. Unfortunately, spherical particles of cross-linked cyclohexylmaleimide-styrene copolymers are quite expensive.

The published European patent application 0,269,324 discloses an organic light diffuser which is suitable

for incorporation into a thermoplastic polymer matrix to form a light-diffusing polymer composition. This light diffuser comprises particles of core/shell morphology which have an average diameter of from 2 to 15 micrometer. The particles have a core of a rubbery alkyl acrylate polymer. The particles have one or more polymer shells, the outer most of which is compatible with the matrix polymer. The shells comprise from 5 to 40% of the weight of the particles. According to the Examples of the European patent application the light diffuser is utilized in amounts of from 2 to 10%, based on the total weight of the polymer composition.

Unfortunately, polymer compositions containing such a high percentage of a light diffuser do not have a very high color stability when exposed to elevated temperatures over an extended period of time.

Therefore, their utility for lighting applications, such as lamp covers, is limited.

One object of the present invention is to provide light diffusers of improved color stability when exposed to elevated temperatures over an extended time period.

One aspect of the present invention is a light diffuser composition comprising

a) from 0.1 to 30 weight parts of inorganic particles having an average particle diameter of from 0.1 to 1 micrometer and a refractive index of from 1.9 to 3.2 and

b) from 1 to 150 weight parts of polymeric particles having a core/shell morphology with a core of a rubbery vinyl polymer and one or more shells, which particles contain at least 15% of a polymerized alkyl acrylate or alkyl methacrylate, based on the total weight of the particles.

The term "average particle diameter" as used herein refers to number average particle diameter.

Another aspect of the present invention is the use of the above-mentioned light diffuser composition for imparting light diffusing properties to a thermoplastic polymer.

Yet another aspect of the present invention is a polymer composition comprising a thermoplastic polymer and

a) from 0.001 to 0.3% of the above-mentioned inorganic particles a) and

b) from 0.01 to 1.5% of the above-mentioned polymeric particles b), based on the weight of the thermoplastic polymer. The polymer composition of the present invention can be in various shapes, for example in the form of a simple mixture of a thermoplastic polymer, the inorganic particles a) and the polymeric particles b) or in the form of pellets or granules or molded articles.

Surprisingly, it has been found that an article produced from a polymer composition comprising a combination of the inorganic particles a) and the polymeric particles b) in the indicated amounts is more resistant to thermal aging than an article produced from a comparable polymer composition containing the polymeric particles b) alone. By "comparable" is meant that the two polymer compositions or articles produced therefrom have similar optical properties, particularly similar total light transmittance and light diffusion. The improved resistance to thermal aging is visualized as improved color stability, i.e. decreased tendency to yellowing when exposed to elevated temperatures over an extended period of time. It has even been found that at a given concentration of polymeric particles b) the color stability increases with increasing concentrations of the inorganic particles a) within the claimed range. This finding is contrary to the experience made with other polymeric light-diffusing particles which do not have core/shell morphology. Polymer compositions containing a combination of inorganic particles a) and said other polymeric light-diffusing particles have found to be less resistant to thermal aging than a polymer composition containing said other polymeric light-diffusing particles alone.

In the practice of producing opalescent polymer compositions it is often desirable that their total light transmittance is in the range from 25 to 50%. When using the above-described polymeric particles b) alone as a light diffuser, the polymer composition generally contains from 4 to 10% of polymeric particles b), based on the weight of the thermoplastic polymer, in order to achieve such a low light transmittance. Such high amounts of polymeric particles b) decrease the color stability of the polymer composition when it is exposed to elevated temperatures over an extended period of time. Furthermore, the viscosity of the polymer composition increases when the concentration of polymeric particles b) in the polymer composition increases. Both problems can be solved by using the inorganic particles a) in combination with the polymeric particles b) and by reducing the concentration of the polymeric particles b) in the opalescent polymer composition. Surprisingly, the improved color stability of the polymer composition of the present invention is not only due to the reduced concentration of the polymeric particles b). Even if the concentration of the polymeric particles b) is kept constant, e.g. at 1 weight-percent, the addition of the inorganic particles a) in an amount within the claimed weight range generally increases the color stability of the polymer composition.

Yet another aspect of the present invention is a process for producing a polymer composition which comprises mixing with a thermoplastic polymer

a) from 0.001 to 0.3% of the above-mentioned inorganic particles a) and

b) from 0.01 to 1.5% of the above-mentioned polymeric particles b),

based on the weight of the thermoplastic polymer,

optionally compounding the mixture to granules or pellets and

optionally producing a molded article from the granules or pellets.

The light diffuser composition of the present invention contains

a) from 0.1 to 30, preferably from 1 to 25, more preferably from 2 to 20 weight parts of inorganic particles having an average particle diameter of from 0.1 to 1 micrometer and a refractive index of from 1.9 to 3.2. and

b) from 1 to 150, preferably from 10 to 120, more preferably from 20 to 100 weight parts of polymeric particles having a core/shell morphology with a core of a rubbery vinyl polymer and one or more shells, which particles contain at least 15% of a polymerized alkyl acrylate or alkyl methacrylate, based on the total weight of the particles.

The weight ratio between the inorganic particles a) and the polymeric particles b) preferably is from 0.5 : 1 to 100 : 1, more preferably $>1 : 1$ to 50 : 1, most preferably 2 : 1 to 25 : 1.

The inorganic particles a) have an average particle diameter of from 0.1 to 1 micrometer, preferably from 0.2 to 0.8 micrometer, most preferably from 0.2 to 0.4 micrometer. Such inorganic particles and methods of producing them are well known in the art. By the term "average particle diameter" the number average is meant.

The inorganic particles have a refractive index of from 1.9 to 3.2, preferably from 2.0 to 2.9, most preferably from 2.0 to 2.7. Preferred inorganic particles a) are titanium dioxide, silica gel, zinc sulfide, zinc oxide or MgTiO_3 particles, provided that their particle size distribution is within the indicated range. The most preferred inorganic particles are titanium dioxide particles. The inorganic particles can be used in the various modifications, for example the anatase, brookite or rutile configuration of titanium dioxide is useful. Titanium dioxide may be coated with a layer of siloxane. Coated titanium dioxide and a method of preparing it is known.

The polymeric particles b) have a core of a rubbery vinyl polymer. The rubbery vinyl polymer can be a homo- or copolymer of any of the monomers having at least one ethylenically unsaturated group which are well known to those skilled in the art to undergo addition polymerization under the conditions of emulsion polymerization in aqueous medium. Such monomers are listed in U.S. patent No. 4,226,752, column 3, lines 40-62, the teaching of which is included herein by reference. The rubbery vinyl polymer preferably contains at least 15%, more preferably at least 25%, most preferably at least 40% of a polymerized acrylate, methacrylate, monovinyl arene or optionally substituted butadiene and from 0 to 85%, more preferably from 0 to 75%, most preferably from 0 to 60% of one or more copolymerized vinyl monomers, based on the total weight of the rubbery vinyl polymer.

Preferred acrylates and methacrylates are alkyl acrylates or alkyl methacrylates which preferably contain 1 to 18, more preferably 1 to 8, most preferably 2 to 8, carbon atoms in the alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec. butyl or tert. butyl or the hexyl, heptyl or octyl groups. The alkyl group may be branched or linear. The preferred alkyl acrylates are ethyl acrylate, n-butyl acrylate, isobutyl acrylate or 2-ethylhexyl acrylate. The most preferred alkyl acrylate is butyl acrylate.

Other useful acrylates are for example 1,6-hexanediol diacrylate, ethylthioethyl methacrylate, isobornyl acrylate, 2-hydroxyethyl acrylate, 2-phenoxyethyl acrylate, glycidyl acrylate, neopentyl glycol diacrylate, 2-ethoxyethyl acrylate t-butylaminoethyl methacrylate, 2-methoxyethyl acrylate, glycidyl methacrylate or benzyl methacrylate.

Preferred monovinyl arenes are styrene or alpha-methyl styrene, optionally substituted at the aromatic ring with an alkyl group, such as methyl, ethyl or tertiary butyl or with a halogen, such as chlorostyrene.

If substituted, the butadiene preferably is substituted with one or more alkyl groups containing 1 to 6 carbon atoms or with one or more halogens, most preferably with one or more methyl groups and/or one or more chlorines. Preferred butadienes are 1,3-butadiene, isoprene, chlorobutadiene, or 2,3-dimethyl-1,3-butadiene.

The rubbery vinyl polymer may contain one or more (co)polymerized acrylates, methacrylates, monovinyl arenes and/or optionally substituted butadienes. These monomers may be copolymerized with one or more other copolymerizable vinyl polymers, such as diacetone acrylamide, vinyl naphthalene, 4-vinyl benzyl alcohol, vinyl benzoate, vinyl propionate, vinyl caproate, vinyl chloride, vinyl oleate, dimethyl maleate, maleic anhydride, dimethyl fumarate, vinyl sulfonic acid, vinyl sulfonamide, methyl vinyl sulfonate, N-vinyl pyrrolidone, vinyl pyridine, divinyl benzene, vinyl acetate, vinyl versatate, acrylic acid, methacrylic acid, N-methyl methacrylamide, acrylonitrile, methacrylonitrile, acrylamide or N-(isobutoxymethyl)acrylamide.

One or more of the above-mentioned monomers are optionally reacted with 0-10%, preferably with 0-5%, of a copolymerizable polyfunctional cross-linker and/or with 0-10%, preferably with 0-5%, of a copolymerizable polyfunctional graftlinker, based on the total weight of the core. If a cross-linking monomer is employed, it is preferably used at a level of from 0.05 to 5%, more preferably from 0.1 to 1%, based on the total weight of the core monomers. Crosslinking monomers are well known in the art and generally have a polyethylenic unsaturation in which the ethylenically unsaturated groups have approximately equal reactivity, such as divinylbenzene, trivinylbenzene, 1,3- or 1,4-triol acrylates or methacrylates, glycol di- or trimethacrylates or -acrylates, such as ethylene glycol dimethacrylate or diacrylate, propylene glycol dimethacrylate or diacrylate, 1,3- or 1,4-

butylene glycol dimethacrylate or, most preferably, 1,3- or 1,4-butylene glycol diacrylate. If a graftlinking monomer is employed, it is preferably used at a level of from 0.1 to 5%, more preferably from 0.5 to 2.5%, based on the total weight of the core monomers. Graftlinking monomers are well known in the art and generally are polyethylenically unsaturated monomers having sufficiently low reactivity of the unsaturated groups to allow significant residual unsaturation to remain in the core subsequent to its polymerization. Preferred graftlinkers are copolymerizable allyl, methallyl or crotyl esters of alpha,beta-ethylenically unsaturated carboxylic acids or dicarboxylic acids, such as allyl methacrylate, allyl acrylate, diallyl maleate, and allyl acryloxypropionate, most preferably allyl methacrylate.

Most preferably, the polymeric particles b) contain a core of a rubbery alkyl acrylate polymer, the alkyl group having from 2 to 8 carbon atoms, optionally copolymerized with from 0 to 5% cross-linker and from 0 to 5% graftlinker, based on the total weight of the core. The rubbery alkyl acrylate is preferably copolymerized with up to 50% of one or more copolymerizable vinyl monomers, for example those mentioned above. Suitable cross-linking and graft-linking monomers are well known to those skilled in the art and are preferably those disclosed in published European patent application 0 269 324.

The core of the polymeric particles b) may contain residual oligomeric material used in the polymerization process to swell the polymer particles, but such oligomeric material has a high enough molecular weight to prevent its diffusion or being extracted during processing or use.

The polymeric particles b) contain one or more shells. Said one or more shells are preferably made of a vinyl homo- or copolymer. Suitable monomers for producing the shell(s) are listed in U.S. patent No. 4,226,752, column 4, lines 20-46, the teaching of which is included herein by reference. One or more shells are preferably a polymer of a methacrylate, acrylate, vinyl arene, vinyl carboxylate, acrylic acid and/or methacrylic acid.

Preferred acrylates and methacrylates are alkyl acrylates or alkyl methacrylates which preferably contain 1 to 18, more preferably 1 to 8, most preferably 2 to 8, carbon atoms in the alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl or tert. butyl, 2-ethylhexyl or the hexyl, heptyl or octyl groups. The alkyl group may be branched or linear. The preferred alkyl acrylate is ethyl acrylate. Other useful acrylates and methacrylates are those listed above for the core, preferably the 3-hydroxypropyl methacrylate. The most preferred alkyl methacrylate is methyl methacrylate.

Preferred vinyl arenes are styrene or alphasubstituted styrene, optionally substituted at the aromatic ring with an alkyl group, such as methyl, ethyl or tertiary butyl or with a halogen, such as chlorostyrene.

A preferred vinyl carboxylate is vinyl acetate.

The shell(s) preferably contain(s) at least 15%, more preferably at least 25%, most preferably at least 40% of a polymerized methacrylate, acrylate or monovinyl arene and 0 to 85%, more preferably 0 to 75%, most preferably 0 to 60% of one or more vinyl comonomers, such as other alkyl methacrylates, aryl methacrylates, alkyl acrylates, aryl acrylates, alkyl and aryl acryl amides, acrylonitrile, methacrylonitrile, maleimide and/or alkyl and aryl acrylates and methacrylates being substituted with one or more substituents, such as halogen, alkoxy, alkylthio, cyanoalkyl or amino. Examples of suitable vinyl comonomers are listed above. Two or more monomers can be copolymerized.

The shell polymer may contain a cross-linker and/or a graft-linker of the type indicated above with respect to the core polymer.

The shell polymers preferably comprise from 5 to 40%, more preferably from 15 to 35%, of the total particle weight.

The polymeric particles b) contain at least 15%, preferably from 20 to 80%, more preferably from 25 to 60%, most preferably from 30 to 50%, of a polymerized alkyl acrylate or methacrylate, based on the total weight of the polymer. Preferred alkyl acrylates and methacrylates are listed above. The alkyl acrylate or alkyl methacrylate constituent can be comprised in the core and/or in the shell(s) of the polymeric particles b). Homopolymers of an alkyl acrylate or methacrylate in the core and/or the shell(s) are useful, however, an alkyl (meth)acrylate is preferably copolymerized with one or more other types of alkyl (meth)acrylates and/or one or more other vinyl polymers, preferably those listed above. Most preferably, the polymeric particles b) contain a core of a poly(butyl acrylate) and one or more shells of poly(methyl methacrylate).

The polymeric particles b) are useful for imparting light diffusing properties to thermoplastic polymers. The refractive index n of core and of the shell(s) of the polymeric particles b) preferably is within ± 0.25 units of, more preferably within ± 0.18 units of, most preferably within ± 0.12 units of the refractive index of the thermoplastic polymer. The refractive index n of the core and of the shell(s) preferably is not closer than ± 0.003 units to, more preferably not closer than ± 0.01 units to, most preferably not closer than ± 0.05 units to the refractive index of the thermoplastic polymer. The refractive index is measured according to ASTM D 542-50 and/or DIN 53400.

The polymeric particles b) generally have an average particle diameter of at least 0.5 micrometer, preferably of at least 2 micrometer, more preferably from 2 to 50 micrometer, most preferably from 2 to 15 micrometer.

By "average particle diameter" the number average is meant. Preferably, at least 90%, most preferably at least 95%, of the polymeric particles b) have a diameter of more than 2 micromet r. The polymeric particles b) are preferably a free-flowing powder.

The polymer particles b) can be produced in a known manner. Generally, at least one monomer component of the core polymer is subjected to emulsion polymerization to form emulsion polymer particles. The emulsion polymer particles are swollen with the same or one or more other monomer components of the core polymer and the monomer(s) are polymerized within the emulsion polymer particles. The swelling and polymerizing steps may be repeated until the particles have grown to the desired core size. The core polymer particles are suspended in a second aqueous monomer emulsion and a polymer shell is polymerized from the monomer(s) onto the polymer particles in the second emulsion. One or more shells can be polymerized on the core polymer. The preparation of core/shell polymer particles is disclosed in published European patent application 0,269,324 and in U.S. patent Nos. 3,793,402 and 3,808,180.

The light diffuser composition of the present invention can be prepared by blending the inorganic particles a) and the polymeric particles b) in the above-indicated weight ratios. The blending can be conducted in an organic diluent. Preferably the dry components a) and b) are blended. Alternatively, the inorganic particles a) can be added prior to or during the production of the polymeric particles b).

The blending temperature is not critical. Room temperature is the most convenient one, however, decreased or elevated temperatures are also useful.

The light diffuser composition of the present invention may contain other inorganic pigments, such as barium sulfate, however, the inclusion of such other inorganic pigments is less preferred. The light diffuser composition of the present invention may contain other organic light diffusers, such as crosslinked poly(methyl methacrylates), polyolefins, MBS-rubbers or another light diffuser described further below. However, the light diffuser composition of the present invention is also very useful in the absence of any significant amounts of other pigments or light diffusers.

The light diffuser composition of the present invention is very useful for imparting light diffusing properties to a thermoplastic polymer .

Accordingly, another aspect of the present invention is a polymer composition containing a thermoplastic polymer and

a) from 0.001 to 0.3%, preferably from 0.01 to 0.25%, most preferably from 0.02 to 0.2% of the above-mentioned inorganic particles a) and

b) from 0.01 to 1.5%, preferably from 0.1 to 1.2%, most preferably from 0.2 to 1.0% of the above-mentioned polymeric particles b),

by the weight of the thermoplastic polymer.

The thermoplastic polymer generally is transparent. It may be clear or colored. Preferably, it is a polyacrylate, a transparent styrene/acrylonitrile copolymer, a polycarbonate or a blend of such a polymers. The light diffuser composition of the present invention is particularly useful for polycarbonates.

In the following paragraphs mainly polymer compositions are described which contain a polycarbonate as a thermoplastic polymer, although the present invention is not limited thereto.

Suitable polycarbonates are described in U.S. patent 4,722,955, column 2, lines 6-42 and the references cited therein. A polycarbonate generally is a polycondensate which is obtainable by reacting a diphenol, such as Bisphenol A and/or bishydroxyphenylfluorene, with phosgene or a diester of a carbonic acid, a dihydroxydiaryalkane, the aryl radicals of which carry one or more methyl groups or halogen atoms in the o- and/or m-position relative to the hydroxyl groups also being suitable, in addition to a unsubstituted dihydroxydiaryalkane. Examples of suitable diphenols which are useful as starting materials for a polycarbonate are listed in U.S. patent No. 4,627,949, column 2, line 68 - column 3, lines 1-22. Most preferably, the polycarbonate is prepared from Bisphenol A and phosgene.

Polycarbonates and methods of producing them are well known in the art. For example the polycarbonate can be prepared by a known interfacial two phase process, a homogeneous organic solution process and/or a melt process. U.S. patent No. 4,092,288 discloses aromatic polycarbonates and methods of preparing them in column 4, lines 4-68 and in Example 1. Alternatively, polycarbonates can be prepared from diphenylcarbonate or dimethyl carbonate by transesterification.

Branched polycarbonates are also suitable. If the polycarbonate is branched, it preferably contains from 0.01 to 3 mole %, more preferably from 0.05 to 2 mole % of a branching agent, by the weight of the polycarbonate. Branched polycarbonates, methods of preparing them and suitable branching agents are for example described in U.S. patent No. 3,544,514, the published European patent application EP-A-0,411,433 and in the references cited in EP-A-0,411,433. A preferred branching agent is 1,1,1-tris(4-hydroxyphenyl)ethane.

The polycarbonates preferably have a number average molecular weight of from 10,000 to 200,000, more preferably from 15,000 to 100,000 and most preferably from 17,000 to 45,000.

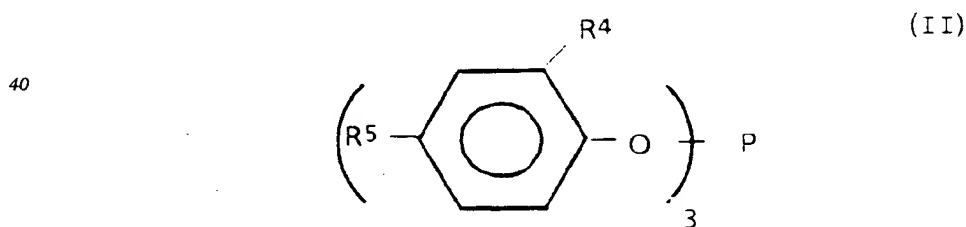
The end groups of the polycarbonate may be the same or different. The most preferred end groups are p-tert-butyl phenyl, p-octyl phenyl, or phenyl. End groups which can lead to a crosslinking of polycarbonate such as arylcyclobutene terminated carbonate polymers are particularly useful. The invention is not restricted to these examples.

5 The polymer composition of the present invention optionally contains an organic light diffuser in addition to the light-scattering polymeric particles b). If present, the amount of an additional organic light diffuser preferably is from 0.01 to 10%, more preferably from 0.02 to 5%, most preferably from 0.5 to 3%, by the weight of the thermoplastic polymer. Exemplary of useful known light diffusers are spherical cross-linked copolymers of 1-90 wt.-% of cyclohexylmaleimide and 99-10 wt.-% of styrene having an average diameter of 4-100 micrometer. Another useful known light diffuser is a poly(methyl methacrylate) resin having an average diameter of 10 0.5-100 micrometer, preferably 1-20 micrometer. The most preferred additional light diffusers are cross-linked homo- or copolymers which contain at least 15 wt.-%, preferably from 20 to 80 wt.-%, more preferably from 25 to 60 wt.-% of a polymerized, optionally alkylated acrylate. If the optionally alkylated acrylate is copolymerized, one or more of the following monomers are preferred for copolymerization: vinyl arenes, such as styrene or an alkyl styrene like methylstyrene or ethyl styrene; olefins, such as butadiene; acrylonitrile or maleimide. 15 Two or more optionally alkylated acrylates can be copolymerized. If alkylated, the acrylate preferably contains a C₁₋₈ alkyl group, more preferably a C₂₋₆-alkyl group. The preferred alkyl acrylates are methyl acrylate, ethyl acrylate and butyl acrylate. These optional organic light diffusers do not have a core-shell morphology. Such organic light diffusers and methods of preparing them are generally known.

20 The polymer composition of the present invention may contain optional additives, such as an optical brightener or fluorescenting dyestuff, a pigment or colorant, tackifier, mold release agent, impact modifier, filler, etc., provided that these optional additives do not have a negative influence on the optical properties of the polymer composition. Such optional additives are generally known in the art. If present, the polymer composition contains an optical brightener, a fluorescenting dye and/or an impact modifier preferably in an amount of from 0.01 to 3 wt.-%. The amount of a pigment or colorant preferably is from 0.0001 to 5 wt.-%, if present at all. Preferred 25 mold release agents are known esters of long fatty acids; their preferred amount is from 0.01 to 2 wt.-%. A preferred filler are glass fibers, their preferred amount is from 1 to 20 wt.-%. All percentages are based on the weight of the thermoplastic polymer.

30 The polymer composition of the present invention may also contain a stabilizer, such as an anti-oxidant and/or a UV stabilizer, such as a sulfur containing molecule, a phosphite, hindered phenol, hypophosphite, phosphonite and/or diphosphonite, such as tetrakis-(2,4-di-tert butylphenyl) biphenylene diphosphonite, etc., which may have been added during the production of the polycarbonate and/or during the production of the polymeric particles b). One or more stabilizers are preferably comprised in the polycarbonate composition in an amount of from 0.01 to 5%, preferably from 0.05 to 2%, by the weight of the polycarbonate.

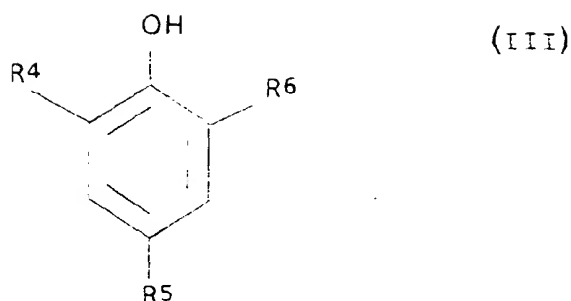
35 A preferred stabilizer is for example an organo-phosphite, preferably a phosphite of formula (II)



wherein R⁴ and R⁵ each independently are a C₁₋₆-alkyl group, a C₁₋₃-hydroxyalkyl group or a C₁₋₃-alkoxy group such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, tert-butyl, a pentyl or a hexyl group, a hydroxymethyl, 50 hydroxyethyl or hydroxypropyl group or a methoxy, ethoxy or propoxyl group. Preferred thereof is tri(2,4-di-tert-butylphenyl)phosphite (IRGAPHOS 168, trademark).

Another preferred stabilizer is a hindered phenol. Hindered phenols and their use as antioxidants are described in Ullmann's Encyclopedia of Industrial Chemistry, Volume 3, "Antioxidants", pages 95-98, 5th ed., 1985, VCH Verlagsgesellschaft mbH and in Encyclopedia of Polymer Science and Engineering, Volume 2, "Antioxidants", pages 75-91, 1985 by John Wiley & Sons, Inc. Methods of preparing the hindered phenols are also 55 well known in the art.

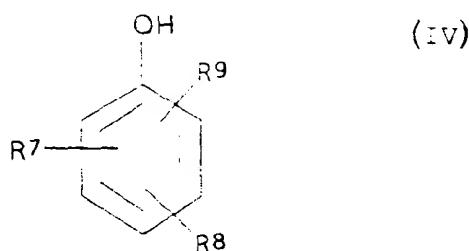
Preferred hindered phenols are those of formula III



wherein R^4 , R^5 and R^6 each independently are a C_{1-6} -alkyl group, a C_{1-3} -hydroxyalkyl group, or a C_{1-3} -alkoxy group such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, tert-butyl, a pentyl or a hexyl group, a hydroxymethyl, hydroxyethyl or hydroxypropyl group or a methoxy, ethoxy or propoxyl group.

Generally at least one, preferably at least two groups should provide steric hindrance to the molecule of formula III. Preferably at least one, more preferably at least two of the groups R^4 , R^5 and R^6 are i-butyl or tert-butyl. Preferred examples of hindered phenols of formula II are 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-sec-butylphenol, 4-(hydroxymethyl)-2,6-di-tert-butylphenol or 2,6-di-tert-butyl-4-methoxyphenol.

Other preferred hindered phenols are those of formula IV



wherein R^7 , R^8 and R^9 are arranged in the ortho and para positions to the hydroxyl group, R^7 is a C_{1-6} -alkyl group, R^8 is a C_{1-6} -alkyl group or a group containing one or more ester, ether, amide, amine, phosphonite, phosphonate, thioester and/or thioether functionalities and containing up to 24, preferably up to 12 carbon atoms, such as the $-CH_2-CH_2-C(O)-O-C_{18}H_{37}$ group or the $-CH_2-S-C_8H_{17}$ group and R^9 is a group containing one or more ester, ether, amide, amine, phosphonite, phosphonate, thioester and/or thioether functionalities and containing up to 24, preferably up to 12 carbon atoms, such as the $-CH_2-CH_2-C(O)-O-C_{18}H_{37}$ group or the $-CH_2-S-C_8H_{17}$ group. When R^7 or R^8 or both are a C_{1-6} -alkyl group, they preferably are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, tert-butyl, a pentyl or a hexyl group.

Preferred examples of hindered phenols of formula IV are octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, commercially available as IRGANOX 1076 (trademark), 2-methyl-4,6-bis((octylthio)-methyl)-phenol, commercially available as IRGANOX 1520 (trademark), 2,6-di-tert-butyl-4-(dimethylaminomethyl)phenol or 3,5-di-tert-butyl-4-hydroxybenzyl di-O-ethyl phosphonate, commercially available as IRGANOX 1222.

Other preferred hindered phenols contain 2 phenolic groups, for example N,N'-1,6-hexamethylenebis-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide, commercially available as IRGANOX 1098 (trademark), 1,6-hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate, commercially available as IRGANOX 259 (trademark), triethylene glycol bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)] propionate, commercially available as IRGANOX 245 (trademark), N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine, commercially available as IRGANOX MD 1024 and nickel or calcium bis[O-ethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate, the latter being commercially available as IRGANOX 1425.

The most preferred hindered phenols are tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane, commercially available as IRGANOX 1010, 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, commercially available as IRGANOX 1076 (trademark) or a 1:1 blend of IRGANOX 1010 and tri(2,4-di-tert-butylphenyl)phosphite (IRGAPHOS 168, trademark), which blend is commercially available as IRGANOX B 225.

The hindered phenol is advantageously utilized in combination with a phosphine of the general formula $PR^1R^2R^3$ (I), wherein R^1 , R^2 and R^3 independently from each other represent an alkyl, cycloalkyl, aryl or aryl-alkyl group or an aryl group which is substituted at the aromatic ring with one or more halogens and/or one or

more alkyl, hydroxy or alkoxy groups.

The radicals R¹, R² and R³ can be identical or different. Of the alkyl groups those are preferred that have 1 to 18, preferably 1 to 12 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, sec. butyl or tert. butyl or the pentyl, hexyl, octyl, nonyl, decyl or octadecyl groups. The alkyl groups can be straight- chain or branched. Of the cycloalkyl groups those having 5 or 6 carbon atoms, such as cyclopentyl or cyclohexyl are preferred. Of the aryl groups those having from 6 to 14 carbon atoms, such as phenyl or naphthyl, are preferred. The aryl groups may be substituted with one or more of the above-mentioned alkyl groups and/or with one or more halogens, such as fluoride, chloride or bromide, and/or one or more hydroxy groups and/or one or more alkoxy groups. Alkoxy groups, if present, preferably contain 1 to 6 carbon atoms, such as the methoxy, ethoxy, n-propoxyl, i-propoxyl, n-butoxyl, sec. butoxyl or tert. butoxyl groups. If substituted, the aryl groups preferably are substituted with 1, 2 or 3 substituent groups. In the aryl-alkyl groups the above-mentioned alkyl groups are preferred and the aryl group preferably is phenyl. Preferred aryl-alkyl groups are benzyl, butyl phenyl or tolyl. Triphenyl phosphine is the most preferred compound of formula (I).

For preparing the polymer composition of the present invention 0.001 to 0.3 wt.-% of the above-described inorganic particles a), 0.01 to 1.5 wt.-% of the above-described polymeric particles b) and, if desired, one or more of the above-mentioned optional additives are mixed with the thermoplastic polymer. These compounds may be premixed before blending the mixture with the thermoplastic polymer. Alternatively, these compounds may be mixed separately with the thermoplastic polymer. The inorganic particles a), the polymeric particles b) and the optional additives may be added simultaneously or in sequence to the thermoplastic polymer. The sequence of addition and the temperature during the addition are not critical. The compounds may be mixed in their undiluted form or one or more of the compounds may be diluted with an aqueous or organic diluent. Instead of preparing a polymer composition containing the above-mentioned concentration of the particles a) and b), master batches can be prepared containing higher concentrations of the inorganic particles a) and polymeric particles b). The master-batches can be blended later with a thermoplastic polymer to prepare polymer compositions containing the claimed concentration of the particles a) and b). It is advisable to mix the inorganic particles a), the polymeric particles b) and the optional additives with the thermoplastic polymer, which may contain optional additives, before the thermoplastic polymer is compounded to granules or pellets. The manner of dispersing or mixing the inorganic particles a), the polymeric particles b) and any optional additives with the thermoplastic polymer(s) is not critical. However, the process chosen should be one which results in a great degree of dispersion of all the additives throughout the thermoplastic polymer. Preferred mixing equipment are mixing rolls, ribbon blenders, dough mixers, Banbury mixers, etc.

The polymer composition can be compounded to granules or pellets by known extrusion techniques. If the polymer composition contains polycarbonate, the extrusion is preferably conducted at a temperature of from 200 to 390°C, more preferably from 250 to 390°C, most preferably from 260 to 380°C. The mixture may be fed into an extruder and extruded to strands which is then comminuted into pellets or granules. Useful extruders are generally known in the art. The extruders generally have a single screw or a double screw. When using a double screw, the screw speed preferably is from 50 to 100 rpm, more preferably from 100 to 350 rpm. When using a single screw, one screw speed preferably is from 5 to 250 rpm, more preferably from 10 to 150 rpm. A preferred compounding method is a devolatilizing extrusion process as generally described in U.S. patent No. 4,627,949 with or without applying a vacuum. The extrusion is generally conducted at a pressure of 0.1 to 100 bar, more preferably at 5 to 60 bar at the extrusion die.

The pellets or granules may be formed into molded articles in a generally known manner, for example by injection-molding, injection blow molding, roll mill processing, rotational molding etc. A preferred processing method is a devolatilizing injection-molding as generally described in U.S. patent No. 4,627,949. If the polymer composition contains polycarbonate, the molding is preferably conducted at a temperature of from 200 to 380°C, more preferably from 250 to 380°C, most preferably from 260 to 380°C.

Examples of molded articles are sheets, films, lamp covers, luminaires, lamps, etc. The molded articles have an excellent surface appearance. The surface is generally very smooth.

The invention is further illustrated by the following examples which should not be construed to limit the scope of the present invention. Unless otherwise mentioned all parts and percentages are weight parts and weight percentages.

Examples 1 to 9 and Comparative Examples A to K

The following components are used for producing the plaques of these examples:

Polycarbonate: In all examples and comparative examples polycarbonate pellets prepared by interfacial polycondensation of bisphenol A and phosgene are used. The polycarbonate has a melt flow rate of 3.3. The polycarbonate pellets are shaken with 1000 ppm of Cetiol 620 S (trademark of Henkel, Germany) as a tackifier

and 1000 ppm of tetrakis-(2,4-di-tert-butylphenyl) biphenylene-diphosphonite, commercially available as Irga-phos-PEPQ (trademark) as an antioxidant. All amounts of the additives are based on the weight of the polycarbonate.

Light diffuser I: a polymer having a core of poly(butyl acrylate) and a shell of poly(methyl methacrylate). The polymer having core/shell morphology is commercially available from Rohm and Haas under the trademark Paraloid EXL 5137. The particle size of the powdered polymer is 2-15 micrometer, the average particle size is 8 micrometer.

Light diffuser II (comparison): a cross-linked copolymer of 58% methyl methacrylate, 39% styrene and 3% cross-linking agent. The polymer is commercially available from Sekisui Plastic under the trademark MSH-8. The polymer has an average particle size of 8 micrometer.

Light diffuser III (comparison): a non-cross-linked acrylate-styrene copolymer. The copolymer is generally used as a matting agent and is commercially available from Degussa under the trademark Degussa OP 278.

Titanium dioxide (TiO₂): having a number average particle size of 0.2 to 0.3 micrometer.

The polycarbonate (containing the above-indicated additives), the light diffuser and, in some examples, titanium dioxide are mixed and then extruded to strands using a Werner and Pfleiderer ZSK 25 mm co-rotating twin screw extruder. The extrusion is carried out under vented conditions at 300 rpm and 60-70 % torque. The amounts of the light diffuser and of titanium dioxide listed in Table 1 below are based on the weight of the polycarbonate. The extrusion temperature is listed in Table 1 below.

Strands are pelletized using a Scherr and Cie 50-E pelletizer. The pellets are injection molded at 300°C into plaques of 3.2 mm thickness. An Arburg Allrounder CMD 370 equipped with a non-vented injection barrel and 35 mm screw is utilized.

The total light transmittance and light diffusion of the plaques are measured according to ASTM D-1003. The test specimens are measured using a Hunterlab Colorquest in transmission mode, utilizing a light source C (daylight simulation), an observer angle of 2° and wave lengths of 400-700 nm.

The color of the produced plaques is measured according to a system defined by the Commission Internationale d'Eclairage (CIE-system) in reflectance (black) according to ASTM E 308. In this system the +L* - axis indicates the brightness, -L* the darkness of the color, +a* the red color component, -a* the green color component, +b* the yellow color component and -b* the blue color component. The components L*, a* and b* are measured prior to and after subjecting the plaques to oven aging at 140°C during 500 hours. The difference between the values b* after and prior to oven aging is calculated and listed in the Table below as delta b. The higher delta b is, the higher is the yellowness of the plaque due to oven aging and the lower is the thermal resistance of the plaque over an extended period of time.

Table 1

(Comp.) Example	Light diffuser (type/%)	TiO ₂ (%)	Total Light Transmittance (%)	Light diffusion	Delta b	Extrusion temp. (°C)
A	I / 0.5	-	69.6	58.1	2.2	315
B	I / 1	-	62.3	52.2	5.3	315
C	I / 2	-	57.5	48.1	5.4	315
D	I / 3	-	55.5	46.3	5.7	315
E	I / 5	-	50.0	41.6	5.7	315
1	I /	0.07	43.7	36.2	3.3	315
2	I / 0.5	0.02	57.7	48.2	4.3	315
3	I / 0.5	0.07	43.9	36.4	3.9	315
4	I / 0.5	0.2	24.6	20.2	3.4	315
5	I / 1	0.02	55.1	46.0	4.6	315
6	I / 1	0.1	37.1	30.7	4.0	315
7	I / 1	0.2	24.4	20.0	3.6	315
F	I / 2	-	58.6	49.1	6.0	365
G	I / 3	-	56.2	47.0	6.3	365
8	I / 0.5	0.02	57.8	48.3	5.2	365
9	I / 1	0.02	57.2	47.8	5.4	365
H	II / 1.5	-	92	79	3.9	365
I	II / 1	0.015	63	52	8.1	365
J	III / 1.5	-	89	51	2.1	365
K	III / 1	0.015	62	46	4.9	365

The comparison between Example 2 (0.5% light diffuser I and 0.02% titanium dioxide) and comparative Example C (2% light diffuser I) illustrates that the plaque of Example 2 has essentially the same total light transmittance and light diffusion as the plaque of comparative Example C but a better color stability (smaller delta b). The comparison between Example 5 (1% light diffuser I and 0.02% titanium dioxide) and comparative Example D (3% light diffuser I) illustrates that the plaque of Example 5 has essentially the same total light transmittance and light diffusion as the plaque of comparative Example D, but a better color stability. Visual inspection of the plaques after oven aging shows that the plaque of Example 2 is whiter than the plaque of comparative Example C and the plaque of Example 5 is whiter than the plaque of comparative Example D. Further, the light diffuser compositions of Examples 2 and 5 respectively are cheaper than the light diffuser in comparative Examples C and D respectively. The same results are achieved when one extrusion of the polymer compositions is conducted at 365°C instead of at 315°C (compare Example 8 with comparative Example F and Example 9 with comparative Example G).

The comparison between comparative Examples A-E illustrates that the color stability during oven aging decreases, i.e. delta b increases when the concentration of the light diffuser I in the plaque increases.

The comparison between Examples 2-4 and 5-7 illustrates that at a given concentration of light diffuser I (0.5 or 1%) the color stability of the plaques during oven aging increases with increasing concentrations of titanium dioxide. This finding is surprising and contrary to the results of comparative Examples H/I and J/K. Although the concentration of the light diffuser II in comparative Example I is smaller than in comparative Ex-

ample H and although only a small amount of titanium dioxide is incorporated into the plaque of comparative Example I, delta b of comparative Example I is substantially higher than delta b of comparative Example H. The same results are observed for comparative Examples J and K.

5 Examples 10 and 11 and Comparative Examples L to P

Polycarbonate pellets prepared by interfacial polycondensation of bisphenol A and phosgene and branched with 0.5% of 1,1,1-tris(4-hydroxyphenyl)ethane are used in these Examples and Comparative Examples. The polycarbonate has a melt flow rate of 3.0. The polycarbonate is heat-stabilized with 1000 ppm of tetrakis-
 10 (2,4-di-tert-butylphenyl) biphenylene-diphosphonite, commercially available as Irgaphos-PEPQ (trademark), based on the weight of the polycarbonate.

The same light diffusers I and III and titanium dioxide are used as described above referring to Examples 1-9. The amounts of the light diffuser and titanium dioxide are listed in Table 2 below.

15 The extrusion and injection molding are conducted in the same manner as described above for Examples 1-9 except that the extrusion temperature is 298°C. The total light transmittance, light diffusion and color stability of the produced plaques are measured in the same manner as described above referring to Examples 1-9.

Table 2

(Comp.) Example	Light diffuser (type/%)	TiO ₂ (%)	Total Light Transmittance (%)	Light diffusion	Delta b
L	I / 0.5	-	70.8	59.6	3.8
25 M	I / 1	-	60.4	51.1	4.75
N	I / 4.5	-	46.9	39.6	5.6
10	I / 0.5	0.05	45.1	38.0	3.5
30 11	I / 1	0.05	43.5	37.1	4.4
O	III / 1	-	86.9	47.5	1.6
P	III / 1	0.05	46.4	39.0	4.6

35 The comparison between Example 10 (0.5% light diffuser I and 0.05% titanium dioxide) and comparative Example N (4.5% light diffuser I) illustrate that the plaque of Example 10 has essentially the same total light transmittance and light diffusion as the plaque of comparative Example N but a substantially better color stability (smaller delta b).

40 The comparisons between Example 10 and Comparative Example L and between Example 11 and Comparative Example M illustrate that even if the concentration of the light diffuser I is kept constant, the addition of titanium dioxide generally decreases delta b, i.e., increases the color stability of the claimed polymer composition.

45 This finding is surprising and contrary to the results of comparative Examples O and P. Delta b of comparative Example P is substantially higher than delta b of comparative Example O. The plaque of comparative Example O has a good color stability, but a total light transmittance which is too high for many lighting applications.

50 Claims

1. A light diffuser composition comprising

- a) from 0.1 to 30 weight parts of inorganic particles having an average particle diameter of from 0.1 to 1 micrometer and a refractive index of from 1.9 to 3.2 and
- 55 b) from 1 to 150 weight parts of polymeric particles having a core/shell morphology with a core of a rubbery vinyl polymer and one or more shells, which particles contain at least 15% of a polymerized alkyl acrylate or alkyl methacrylate, based on the total weight of the polymeric particles.

2. The light diffuser composition of claim 1 wherein the rubbery vinyl polymer of the core of the polymeric particles b) contains at least 15% of a polymerized acrylate, methacrylate, monovinyl arene or optionally substituted butadiene and from 0 to 85% of one or more copolymerized vinyl monomers, based on the total weight of the rubbery vinyl polymer.
- 5 3. The light diffuser composition of claim 1 wherein the polymeric particles b) contain a core of a rubbery alkyl acrylate polymer, the alkyl group having from 2 to 8 carbon atoms, optionally copolymerized with from 0 to 5% cross-linker and from 0 to 5% graftlinker, based on the weight of the core, and one or more shells containing a polymer of a methacrylate, acrylate, vinyl arene, vinyl carboxylate, acrylic acid and/or methacrylic acid, the shells comprising from 5 to 40% of the weight of the particles.
- 10 4. The light diffuser composition of any one of claims 1 to 3 wherein the weight ratio of the polymeric particles b) to the inorganic particles a) is from 0.5 : 1 to 100 : 1.
- 15 5. The light diffuser composition of any one of claims 1 to 4 wherein the inorganic particles a) are titanium dioxide, silica gel, zinc sulfide, zinc oxide or MgTiO_3 .
6. Use of the light diffuser composition of any one of claims 1 to 5 for imparting light diffusing properties to a thermoplastic polymer.
- 20 7. A polymer composition comprising a thermoplastic polymer and
a) from 0.001 to 0.3% of the inorganic particles a) as defined in claim 1 or claim 5 and
b) from 0.01 to 1.5% of the polymeric particles b) as defined in any one of claims 1 to 3, based on the weight of the thermoplastic polymer.
- 25 8. The polymer composition of claim 7 comprising
a) from 0.01 to 0.25% of the inorganic particles a) and
b) from 0.1 to 1.2% of the polymeric particles b), based on the weight of the thermoplastic polymer.
9. The polymer composition of claim 7 or claim 8 wherein the thermoplastic polymer is a polycarbonate.
- 30 10. The polymer composition of any one of claims 7 to 9 in the shape of granules, pellets or a molded article.
11. A process for producing the polymer composition of any one of claims 7 to 10 which comprises mixing with a thermoplastic polymer
a) from 0.001 to 0.3% of the inorganic particles a) as defined in claim 1 or claim 5 and
35 b) from 0.01 to 1.5% of the polymeric particles b) as defined in any one of claims 1 to 3, based on the weight of the thermoplastic polymer, optionally compounding the mixture to granules or pellets and optionally producing a molded article from the granules or pellets.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5105

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 474 203 (FERRO ENAMELS (JAPAN) LIMITED) * page 6, line 47 - line 55; claims; examples 6-9 *	1	C08K3/00 C08L51/06 C08L69/00 G02B5/02
A	--- CHEMICAL ABSTRACTS, vol. 109, no. 10, 5 September 1988, Columbus, Ohio, US; abstract no. 74390t, & KAGAKU KOGYO, vol. 39, no. 5, 1988 pages 415 - 421 KUNIO FURUSAWA 'Functional polymer emulsions - their new development'	1	
A	--- DATABASE WPI Week 9231, Derwent Publications Ltd., London, GB; AN 92-256536 & JP-A-4 175 351 (TOA GOSEI CHEM. IND., LTD) 23 June 1992 * abstract *	1	
A	--- CHEMICAL ABSTRACTS, vol. 119, no. 4, 26 July 1993, Columbus, Ohio, US; abstract no. 29205g, * abstract * & JP-A-4 309 528 (TOA GOSEI CHEMICAL INDUSTRY CO., LTD.) 2 November 1992	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08K C08L G02B
A	--- CHEMICAL ABSTRACTS, vol. 118, no. 26, 28 June 1993, Columbus, Ohio, US; abstract no. 256247v, * abstract * & JP-A-4 256 345 (TOA GOSEI CHEMICAL INDUSTRY CO., LTD) 11 September 1992	1	
D,A	--- EP-A-0 269 324 (ROHM AND HAAS COMPANY) * claims *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 September 1994	Examiner DE LOS ARCOS, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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Durable multilayer coating.

A laminate comprises, in consecutive order, a metal substrate, with or without a primer layer for powder coating ; a powder coating layer and a fluorine resin top coat ; in which the powder coating layer is formed by applying onto the metal substrate (with or without a primer layer), a composite powder coating composition containing mother powder particles comprising a film-forming binder resin which is solid at room temperature and heat-meltable and a pigment, together with microparticles of a resin containing, as an essential component, methyl methacrylate and having an average diameter of 0.001 to 10 μ m, in an amount of 0.05 to 40% by weight of the total powder coating composition ; and then baking the formed coating.

EP 0 460 973 A2

The present invention relates to a durable laminate and more specifically, a super-durable laminate comprising in consecutive order, a metal substrate, a powder coating layer and a fluorine resin top coat, the laminate being specifically excellent in interlaminar adhesion and showing the desired properties of said powder coating and fluorine resin coat in full.

Though a top coat composition based on a fluorine resin is useful in giving a coating with excellent weather resistance and corrosion resistance, but is very poor in adhesion towards substrate or under coat on said substrate. Therefore, in the actual application as in colored steel plate for roofing material and the like, an epoxy resin which is excellent in adhesion towards substrate and in processability, is first applied on as a surface primer coating, on which a fluorine resin based coating composition is applied to have a laminated coating. However, heretofore proposed epoxy primer compositions are all solvent type coating compositions, resulting coatings with at most about 5 microns thickness. Therefore, should the coating be mechanically damaged during transportation or processing step, cut would often reach to the substrate, resulting a marked loss in corrosion resistance of the coating. It is hardly possible to prepare the thicker coating with this solvent type epoxy primer coating composition without the fear of occurrence of cracks, sagging and the like.

On the other hand, a powder coating is in general believed to be suitable for thicker coating, and however, in the combination of fluorine resin coating and powder coating, it is generally poor in interlaminar adhesion and especially in the case of epoxy powder coating, such combination has never been practically used because of their extremely poor interlaminar adhesion properties.

Under the circumstances, the inventors have previously found a surprising fact that adhesion of fluorine resin coating towards powder coating is greatly improved when a particular powder coating composition comprising a particular epoxy resin, i.e. bisphenol A type epoxy resin, and a particular hardening agent, i.e. phenolic hardening agent, is selectively used as said powder coating and applied for patent on it (as Japanese Patent Application No. 196133/87, now published as Publication (unexamined) No. 40329/89). In that invention, a thicker powder coating based on an epoxy resin having comparatively good processing properties is first applied on said primer coating, and the interlaminar adhesion between the coatings is likewise excellent.

Therefore, the resulted laminate is specifically useful as roofing material and others which require improved corrosion resistance under severe environmental conditions. However, the powder coating for the said epoxy primer coating was only limited to the composition comprising a particular epoxy resin and a particular hardening agent and there was additional problem of resulting only matte surface coating. It is, therefore, an object of the invention to provide a laminate comprising in consecutive order, a metal substrate, a powder coating layer and a fluorine resin top coat, the powder coating being freely selected from various kinds depending on the properties desired and the resulted laminate being excellent in interlaminar adhesion and properties and especially durability.

An additional object of the invention is to provide a super-durable laminate which is far excellent in processability, corrosion resistance and weather resistance as compared with those of heretofore proposed laminates.

Summary of the invention

According to the invention, the abovementioned objects may be attained with a laminate consisting, in consecutive order, of a metal substrate with or without a primer layer for powder coating, a powder coating layer and a fluorine resin top coat, characterized in that the powder coating layer is formed by applying onto the metal substrate with or without a primer layer, a composite powder coating composition comprising mother powder particles comprising a film-forming binder resin which is solid at room temperatures and heat-meltable and pigment, added with microparticles of a resin containing as an essential component methyl methacrylate and having an average diameter of 0.001 to 10 microns, in an amount of 0.05 to 40 % by weight of the total powder coating composition, and then subjecting the formed coating to a baking, thus formed powder coating layer being specifically excellent in durability.

In this invention, such metal plate as steel plate, galvanized steel sheet, aluminium plate, aluminium-galvanized steel sheet, stainless steel sheet and the like, with or without a primer for powder coating can be advantageously used as a substrate. As the primer, any of the known primers for powder coating, based on polyester resin, epoxy resin, acrylic resin, urethane resin or the like may be satisfactorily used as desired.

The powder coating to be applied on said substrate comprises mother powder particles based on a film-forming binder resin which is solid at room temperatures and is heat-meltable, added with microparticles of a resin containing as an essential constituting monomer methyl methacrylate, and having an average diameter of 0.001 to 10 microns. The amount of said resin microparticles may be in a range of 0.05 to 40% by weight, preferably 0.1 to 20% by weight of the total weight of the composite powder coating.

This adding amount may be cut in proportion to the decrease in average diameter of said resin micropar-

ticles, and however, from the standview of production easiness, the lower limit of the average diameter of said microparticles should be about 0.001 micron. At that particle size, about 0.05% by weight to the total weight of the composite powder coating of such microparticles should be added to secure the intended objects and effects of the present invention. If the particle size exceeds over the upper limit of 10 microns, then the amount of resin microparticles should be increased up to more than 40% by weight for better adhesion toward a top coat applied. However, at that time, there results adverse effects on the coating appearance and the like and hence, such a higher amount should be avoided in the present invention.

As the binder resin of the mother powder particles, any of the known film-forming resins which are solid at room temperatures and heat-meltable, as acrylic resin, polyester resin, epoxy resin and the like may be successfully used. To this binder resin, pigment, hardening agent and other conventional additives may be optionally added. There is no particular limit on the average diameter of such mother powder particles and however, preference is given to a range of 30 to 50 microns, from the standviews of application characteristics, coating surface appearance and the like. The present microparticles may be composed of any kind of resins providing containing methyl methacrylate component. However, from the production and practical points of view, preference is given to such resin as vinyl resin (including acrylic resin), epoxy resin, polyester resin, melamine resin and the like, and especially vinyl resin. The last-mentioned resin is specifically preferred, because it is easily prepared by varying its composition at will. Thus, a various combination of polymerizable vinyl monomers may be directly polymerized by using an emulsion polymerization, suspension polymerization or the like, to obtain the resin microparticles or such monomers may be polymerized by means of solution polymerization, mass polymerization or the like and thus obtained resin is pulverized and shieved. The resin microparticles may be of either crosslinked or non-crosslinked type and the particles may have spherical, fibrous or plate form.

In preparing vinyl resin microparticles, methyl methacrylate is essential in this invention and however, the following vinyl monomers may be advantageously co-used each separately or in the combination of 2 or more, i.e. 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, polyethyleneglycol mono(meth)acrylate, polypropyleneglycol mono(meth)acrylate, (meth)acrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, glycidyl (meth)acrylate, -methyl glycidyl (meth)acrylate, N-glycidyl acrylamide, vinyl sulfonic acid glycidyl, (methyl) glycidyl ether of allyl alcohol and the like.

Besides them, the following may be used as desired, i.e. methyl acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, 2-ethyloctyl (meth)acrylate, dodecyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, dialkyl fumarate, dialkyl itaconate, styrene, (meth) acrylonitrile, vinyl toluene, -methyl styrene, (meth) acrylamide, methylol (meth) acrylamide, vinyl acetate, vinyl propionate, lauryl vinyl ether, halogen-containing vinyl monomers and the like. Regarding an average grain diameter of such resin microparticles, there is no particular conditions, providing being smaller than the average diameter of mother powder particles and however, for the reasons hereinbefore stated, it should preferably be in a range of 0.001 to 10 microns and more preferably 0.01 to 5 microns.

The present resin microparticles are thus characterized by containing as an essential constituting component methyl methacrylate. The content of this particular monomer in said resin is not absolutely limitative, but rather fluctuate depending on the properties of binder resin, mixing easiness and the like. It is, however, preferred to select in a range of 10 to 100%, in solid weight ratio, of the total resin weight.

In the present powder coating, the abovementioned resin microparticles are contained so that the microparticles are present at least on the surface of the respective mother powder particles. For this end, the resin microparticles are added to the mother powder particles at any stage of the preparation of the latter particles.

To corroborate the fact that resin microparticles are maintained in solid form and located on the surface of the respective mother powder particles, in the most preferable embodiment, the resin microparticles are added with the mother powder particles. Addition of resin microparticles to the mother powder particles may be carried out by using various mixing measures. In the first method, the mother particle resin, hardening agent and optional pigment and other additives are melt-kneaded and during or after pulverization step, the resin microparticles are mixed in Super mixer, Henshel mixer or the like. In the second method, the mother powder particles obtained by wet dispersion means and the resin microparticles are mixed well in Hybritizer, Ball mill or the like. In another method, the mother particles are coated with the resin microparticles and fused to form a continuous film thereupon.

Therefore, the term "contain" as used herein shall denote every embodiments as herein above mentioned. However, the invention can never be limited in any sense by the preparation method used, and it is also possible to have the composite powder coating by using a comparatively larger quantity of resin microparticles in, for example, melting or granulating step of powder particles, thereby placing the resin microparticles at least on the surface of the respective mother powder particles, or by using the combination of said processes.

Though the mixture form may somewhat vary with the addition method used, this shall give no influence for the essential features of the present invention.

Thus obtained powder coating composition as applied by conventional application means on the surface of substrate and then over-coated with a fluorine resin. As already stated, adhesion of fluorine resin toward powder coating is in general no good and this is especially in the case of vinylidene fluoride type fluorine resin because of having no adhering functional groups. However, with the present powder coating composition, said adhesion is excellent, resulting an improved durable fluorine resin over coat.

The invention shall be now more fully explained in the following Examples and comparative Examples.

Unless otherwise being stated, all parts and percentages are by weight.

Synthetic Example 1 (Synthesis of resin microparticles A)

Into a reaction vessel fitted with a stirrer, a condenser, and a thermoregulator, were placed 380 parts of deionized water and 2 parts of nonionic surfactant MON2 (manufactured by Sanyo Kasei) and heated under stirring to 80°C to have a solution. To this, was added a solution of 1 part of ammonium persulfate (initiator) in 10 parts of deionized water and then dropwise added in 60 minutes a mixture of 61 parts of methyl methacrylate, 36 parts of styrene and 3 parts of n-butyl methacrylate. After completion of said addition, the combined was stirred at 80°C for 60 minutes to obtain an emulsion having a non-volatile content of 20% and an average particle diameter of 0.03 to 0.05 μ . This emulsion was spray-dried to obtain resin microparticles A.

Synthetic Example 2 (Synthesis of resin microparticles B)

Into a reaction vessel fitted with a stirrer, a condenser and a thermoregulator, were placed 380 parts of deionized water and 2 parts of nonionic surfactant MON2 (manufactured by Sanyo Kasei) and heated under stirring to 80°C to obtain a solution. To this, was added a solution of 1 part of ammonium persulfate (initiator) in 10 parts of deionized water and then dropwise added in 60 minutes a mixture of 90 parts of methylmethacrylate, 33 parts of styrene, 46 parts of n-butyl methacrylate, and 20 parts of 2-hydroxyethyl methacrylate. After completion of said addition, the combined was further stirred at 80°C for 60 minutes to obtain an emulsion having a non-volatile content of 20% and an average particle diameter of 0.03 to 0.05 μ .

This emulsion was subjected to spray-drying to obtain resin microparticles B.

Synthetic Example 3 (Synthesis of resin microparticles C)

Into a reaction vessel fitted with a stirrer, a condenser and a thermoregulator, were placed 380 parts of deionized water and 2 parts of nonionic surfactant MON2 (manufactured by Sanyo Kasei) and heated under stirring to 80°C to obtain a solution.

To this, was added a solution of 1 part of ammonium persulfate (initiator) in 10 parts of deionized water and then dropwise added in 60 minutes a mixture of 3 parts of lanryl methacrylate, 15 parts of methylmethacrylate and 82 parts of styrene. After completion of said addition, the combined was stirred at 80°C for 60 minutes to obtain an average particle diameter of 0.03 to 0.05 μ . This emulsion was then subjected to spray-drying to obtain resin microparticles C.

Synthetic Example 4 (Synthesis of pulverized resin microparticles D)

Into a flask fitted with a dropping funnel, a stirrer and a thermometer, were placed 80 parts of xylene and heated to 130°C.

Using the dropping funnel, a mixture of 36 parts of methyl methacrylate, 10 parts of styrene, 24 parts of glycidyl methacrylate, 30 parts of t-butyl methacrylate and 6 parts of Kayaester O (initiator) was dropwise added at a constant speed in 3 hours to the flask and after standing for 30 minutes, a solution of 1 parts of Kayaester O in 20 parts of xylene was added in 1 hour. Thereafter, the combined was maintained at 130°C for additional 2 hours and then the solvent was distilled an acrylic resin. Thus obtained acrylic resin was pulverized to obtain non-crosslinked resin microparticles D having an average diameter of 30 μ .

Synthetic Example 5 (Preparation of epoxy coating composition E)

100 parts of Epotohto YD-019 (epoxy resin, manufactured by Tohto Kasei), 3 parts of dicyandiamide and 40 parts of Titanium oxide CR50 were dry-mixed in Henshel Mixer (trade mark, Mitsui-Miike Seisakusho) and then the content was melt-dispersed at 100°C in Cokneader PR-46 (trade mark, Bus Co., Swiss).

After cooling, the resin mass obtained was pulverized by using Hammer mill and shieved by using 150 mesh metal net to obtain mother powder particles E.

Synthetic Example 6 (Preparation of polyester coating composition F)

100 parts of ER 6800 (polyester resin, manufactured by Nippon Polyester Co.), 36 parts of Kureran U1 (blocked isocyanate, manufactured by BASF) and 40 parts of Titanium oxide CR50 were dry-mixed in Henshel Mixer and then melt-dispersed at 100°C by using Cokneader PR-46 (Bus, Swiss). After cooling, thus obtained resin mass was pulverized by using Hammer mill and then shieved by using 150 mesh metal net to obtain mother powder particles F.

Example 1

In Henshel mixer, 99.95 parts of the mother powder particles E obtained in Synthetic Example 5 and 0.05 parts of the resin microparticles A were dry-mixed for 30 seconds to obtain composite powder coating composition.

Thus obtained powder coating composition was applied on a steel sheet by using an electrostatic spray equipment and the coating was baked at 180°C for 20 minutes to obtain a coating with 80 micron thickness.

On this coating, Duraner C (fluorine coating composition, trade mark, Nippon Paint Co., Ltd) was applied by using a bar coater and then baked at 270°C for 1 minute to obtain a top coat with 20 micron thickness.

Thus obtained laminate was tested in respect of coating appearance and interlaminar adhesion between the powder coating layer and fluorine resin coating and test results were shown in Table 1. In every respects, the test results were excellent.

Examples 2-8

Following the procedures of Example 1, various composite powder coating compositions were prepared and applied on test substrates. Thereafter, fluorine resin coatings were prepared as in Example 1. The similar tests were conducted and test results were shown in Table 1. In every Examples, test results were excellent.

Comparative Example 1

Similar composite powder coating composition was prepared with the materials shown in Table 1 and the similar was prepared.

However, in this experiment, there resulted poor adhesion between the powder coating layer and the fluorine resin layer.

Comparative Examples 2-4

Following the procedures of Comparative Example 1, but using the materials shown in Table 1, various comparative composite powder coating compositions and experiments, the coatings were no good because of having poor levelling properties.

Table 1 (1)

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Example No.	1	2	3	4	5
Mother powder resin	E p o x y				
resin microparticles	A	B	C	A	A
Adding amount of resin microparticles	0.05	0.1	0.1	10	40
average diameter of microparticles	0.05	0.05	0.05	0.05	0.05
Inter laminar adhesion with fluorine resin coating	○	◎	◎	◎	◎
levelling property	◎	◎	○	◎	○

40

Adding amount weight of resin microparticles
of resin = weight of the composite powder coating
microparticles

45

50

Inter laminar = tested by cross-cut adhesion test
adhesion ◎ 100/100
 ○ 100/ 90 or more
 X 100/ 50 or less

55

Table 1 (2)

5

10

15

20

25

30

35

Example No.	6	7	8
Mother powder resin	Polyester		
resin microparticles	C	C	C
Adding amount of resin microparticles	0.1	10	40
average diameter of microparticles	0.05	0.05	0.05
Inter laminar adhesion with fluorine resin coating	◎	◎	◎
levelling property	◎	◎	○

40

Adding amount of resin microparticles = $\frac{\text{weight of resin microparticles}}{\text{weight of the composite powder coating microparticles}}$

45

50

Inter laminar adhesion = tested by cross-cut adhesion test

◎ 100/100

○ 100/ 90 or more

✕ 100/ 50 or less

55

Table 1 (3)

Comp.Ex.	1	2	3	4
Mother powder resin	Polyester			
resin microparticles	A	D	C	C
Adding amount of resin microparticles	0.003	0.1	60	60
average diameter of microparticles	0.05	30	0.05	0.05
Inter laminar adhesion with fluorine resin coating	X	○	⊙	⊙
levelling property	⊙	X	X	X

Adding amount $\frac{\text{weight of resin microparticles}}{\text{weight of the composite powder coating microparticles}}$
of resin

Inter laminar = tested by cross-cut adhesion test

adhesion ⊙ 100/100

○ 100/ 90 or more

X 100/ 50 or less

Claims

1. A laminate comprising, in consecutive order, a metal substrate, with or without a primer layer for powder coating; a powder coating layer and a fluorine resin top coat; in which the powder coating layer is formed by applying onto the metal substrate (with or without a primer layer), a composite powder coating composition containing mother powder particles comprising a film-forming binder resin which is solid at room temperature and heat-meltable and a pigment, together with microparticles of a resin containing, as an essential component, methyl methacrylate and having an average diameter of 0.001 to 10 μm , in an amount of 0.05 to 40% by weight of the total powder coating composition; and then baking the formed coating.
2. A laminate according to claim 1, wherein the binder resin is an acrylic resin, polyester resin or epoxy resin.
3. A laminate according to claim 1 or claim 2, wherein the fluorine resin is a vinylidene fluorine polymer.
4. A laminate according to any one of the preceding claims wherein the primer layer, when preset, is composed of a polyester resin, epoxy resin, acrylic resin or urethane resin.

